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The present invention provides methods for the identification ligand compounds that bind to target molecules such as proteins or structured RNA with as little as millimolar (mM) affinity using mass spectrometry. The methods may be used to determine the mode of binding interaction between two or more of these ligand compounds to the target as well as their relative affinities. Also provided are methods for designing compounds having greater affinity to a target molecule by identifying two or more ligands using mass spectrometry methods of the invention and linking the ligands together to form a novel compound.